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Effects of non-hydrostatic pressure on electrical resistance of bundled single-wall carbon nanotubes

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Abstract. Recent studies have shown that single wall carbon nanotubes (SWCNT) exhibit a sequence of phase transitions and demonstrate a high structural stability up to 35 GPa of quasi-hydrostatic pressure [1] beyond which an irreversible structural transformation occurs. Here we report on the study of electrical resistance of SWCNTs at pressures up to 34 GPa in the temperature range of 293 – 395 K. In the pressure range 10-25 GPathe rate of resistance change decreases considerably. We associate such behavior of the resistance with a structural modification of the SWCNTs or/and change of the conductivity character at high pressure. Raman spectra of the samples recovered after 30 GPa exhibit a large increase of defect concentration in the CNTs. Isobaric temperature dependences of the CNT resistance R(T) measured in the temperature range 300-400 K reveal some changes with pressure whereas the semiconducting character of the R(T) remains unaltered.

1. Introduction

According to recent experimental data [1,2], single wall carbon nanotubes exhibit a sequence of structural transitions and demonstrate a high structural stability up to 35 GPa of quasi-hydrostatic pressure. The authors [1] tentatively relate an irreversible transformation of SWCNTs which occurs above 35 GPa to theoretically predicted polymerization of the material [3]. Change of CNTs structure at high pressure/stress may affect profoundly the electronic properties of nanotubes and even cause semiconducting to metal (and vice versa) transition [4]. Whereas several important Raman studies addressing the problem of SWCNTs [1,2] and DWCNTs [5, 6] integrity at high pressure have been recently reported they suffer from a common problem - only a fraction of the CNTs resonant with the laser excitations used in these experiments has been followed. This drawback can be eliminated by following evolution of CNTs' transport properties at extreme pressure as that will probe the entire nanotube ensemble. Importantly, no measurements of electrical transport properties of CNTs at high pressure/stress have been conducted to date. Here we report on the study of electrical resistance of SWCNTs at non-hydrostatic pressures up to 34 GPa in the temperature range of 300 – 400 K and correlate the results with correspondent structural changes of nanotubes.

2. Experimental methods

In this work we used purified CNTs which had been produced by HiPCO method by Tubes @ Rice Ltd. This type of nanotubes offers an advantage of a wide range of tube diameters typically ranging from 0.7 to 1.3 nm thus allowing probing a response of very different CNT species to the extreme pressure/stress. A certain amount of residual metal catalyst remains in the material as evidenced from the transmission electron microscopy (TEM) analysis (figure 1). Raman characterization of the material before and after high-pressure experiments was done on NTEGRA Spectra probe nanolaboratory confocal microscope from NT MDT, with He-Ne excitation laser (632 nm). The spectra were collected in back scattering geometry with resolution of 2.3 cm^{-1}. A 100x objective with a numeric aperture of 095 was used for focusing. Laser power was measured directly on the microscope sample stage and did not exceed 5mW. A typical Raman spectrum of the source material collected at ambient conditions (figure 1) displays the main features of CNTs, radial breathing mode (RBM) at low frequencies (from 150 to 300 cm^{-1}), D-band (characteristic of defects on the nanotube surface) and G-band at 1350 cm^{-1} and at 1600 cm^{-1}respectively. One should notice the relative low intensity of D band in comparison to G band which is indicative of low defect density in purified HiPCO CNTs used in this study.

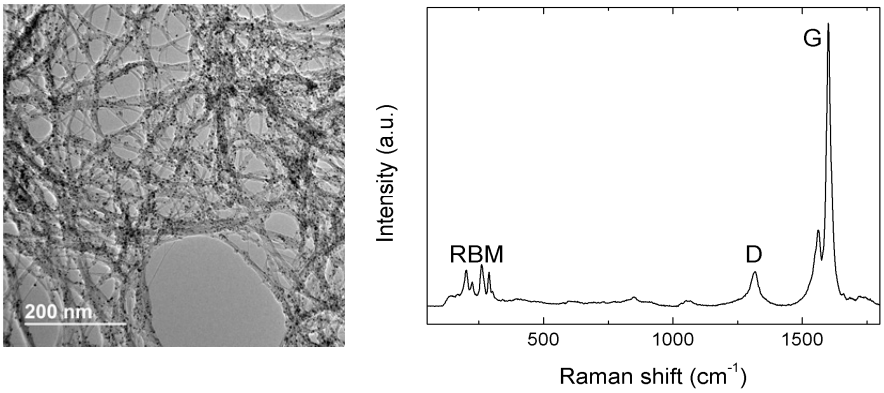

Figure 1.TEM image (left panel) and Raman spectrum of HiPCO CNTs collected at ambient conditions (right panel). RBM, D- and G-band are indicated.

High pressure was generated in a cone-plane cell (figure 2) with anvils made of carbonado type diamond [7,8] which allow for resistance measurements under pressures up to 50 GPa [9]. A cross section of the contact area between the anvils and the sample under investigation is typically around 200 μm. The sample thickness after pressure-induced compactization is approximately 10 μm. Pressure in the cell was determined from the applied load using calibration data for reference materials with error not exceeding 10% in the pressure range of 5-50 GPa [9]. First, the CNT sample was pressurized about 30 GPa with subsequent pressure release followed by a second pressure cycle which was conducted in order to examine reversibility of the R(p) dependence. CNT resistance dependence on temperature R(T) was measured between 300 and 400 K at two selected pressures (20 and 30 GPa). Temperature uncertainty was about 0.1 K

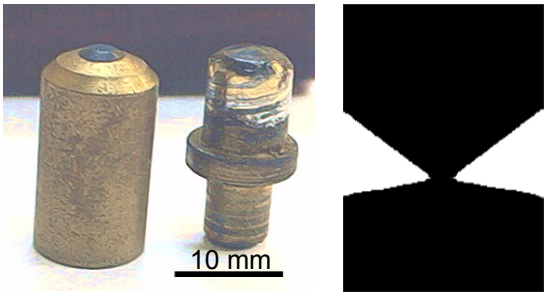

Figure 2. The conductive (carbonado) diamond anvils (left panel) and schematic cross-section of the plane – cone pressure cell (right panel), not to scale

3. Results and discussion

3.1. Pressure dependence of electrical resistance of SWCNTs

The electrical resistance decreases as pressure is increased from about 80 Ohm at 12 GPa to less than 30 Ohms at 28 GPa for the first pressure cycle (figure 3), The resistance evolution with pressure shows a first anomaly at approximately 16 GPa and another one at around 25 GPa. This first irregularity appears at the pressure corresponding to the collapse pressure Pc of the CNTs with the largest diameter (1.3 nm). In addition, the second change in the pressure dependence of electrical resistance is also related to the structural change of the large tubes, as 25 GPa corresponds to the collapse pressure of tubes with a diameter of 1.1 nm.

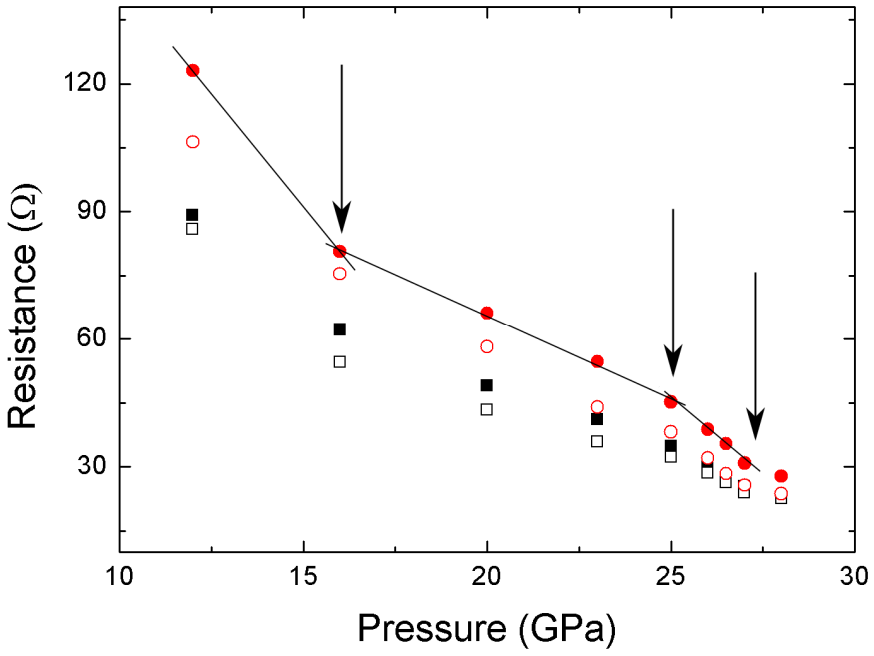

Figure 3. Pressure dependence of the resistance of the SWCNTs nanotubes for the cycle 1 (squares) and cycle 2 (circles). Solid and open symbols represent data collected on pressure increase and release respectively. Straight lines indicate quasi-linear character of the R(p), see text.

Theoretical calculations predict collapse of CNTs in bundles at high pressure [8]. The collapse pressure P_c depends on the CNT diameter d as $P_c = k/d^3$ where k is a constant. Experimental studies [2,8] report on CNT collapse at high pressure in accordance to the theoretically predicted dependence

on nanotubes' diameter. Using the data on the SWCNT collapse [2,8] we estimated the collapse pressures range for SWCNT used in our study to be 16 - 100 GPa in accordance to the above mentioned formula for P_c with the highest P_c corresponding to CNTs with the smallest diameter (0.7 nm). The pressure range of our experiment falls into this interval and therefore it is reasonable to associate the peculiarities in R(p) dependence with sequential collapse of the nanotubes at correspondent P_cs on pressure increase. From the latter we can define diameters of the nanotubes which undergo this structural transformation. Our estimation gives CNT diameters of 1.3, 1.1 and 1.08 nm for P_cs 16, 25, and 27 GPa respectively. A 10% hysteresis in R(p) observed upon pressure release (figure 3) is probably connected to delay in the CNT shape recovery after collapse.

3.2. Temperature dependence of electrical resistance of SWCNTs at different pressures

Carbon nanotubes can be metallic or semiconducting depending on their chirality. In order to examine the overall electronic properties of the CNT material we performed isobaric measurements of the sample resistance in temperature interval 295 – 400 K at 20 and 30 GPa selected from the pressure interval before and after P_c = 25 GPa respectively. The observed temperature dependences of the resistance R(T) exhibit similar qualitative behavior (figure 4) – the resistance increase with decreasing T typical of semi-conducting material, implying that more than 30% of the CNT species in the sample are semiconducting. The R(T) dependencies are non-linear in ln(R) – 1/T coordinates below 370 K implying Ahrenius mechanism of electrical conductance does not hold in the entire T-range of our experiment (right panel of figure 4). Importantly, the character of R(T) at 30 GPa differs from that at 20 GPa. As certain fraction of CNTs undergo pressure-induced collapse at P_c = 25 GPa (figure 3) it is reasonable to associate altering the overall R(T) dependence with electrical conduction mechanism and gap change in the collapsed (flattened) CNTs. We even can not exclude the occurrence of semiconductor to metal transition in some CNTs caused by stress [4] although such transition is not dominant in the studied pressure range and thus can not be identified on the background of rest of the CNT ensemble.

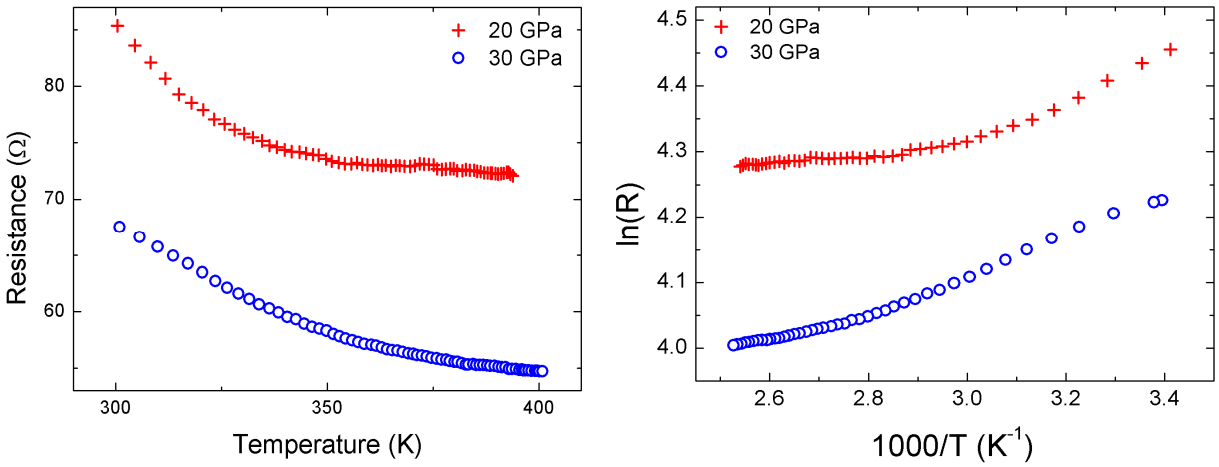

Figure 4. Temperature dependences of the SWCNT resistance R at selected pressures (left panel) and lnR vs 1/T plot (right panel). Crosses and circles – data for 20 and 30 GPa respectively.

3.3. Spectroscopic characterization of SWCNTs recovered from high-pressure

SWCNTs exposure to high pressure resulted in dramatic changes in their Raman spectra (figure 5). Specifically, the D-band to G-band peak intensity ration (I_D/I_G) has increased from 0.6 to 1 implying introduction of more structural defects on the CNTs surface. This result implies that a substantial fraction of the nanotubes has undergone collapse during the pressure cycling as it was shown in [6] the generation of new structural defects on nanotubes surface occurs when they are in a collapsed state. It

is important to underscore that nevertheless, the RBM band remains essentially unaltered: the main peaks at 200, 252, 261, 288 and 301 cm^{-1} are still visible and display the same shape and relative intensity after two consecutive pressure cycles to 30 GPa. That testifies for the CNTs full recovery after the pressure cycling – neither irreversible structural transformation, nor polymerization of the tubes has occurred.

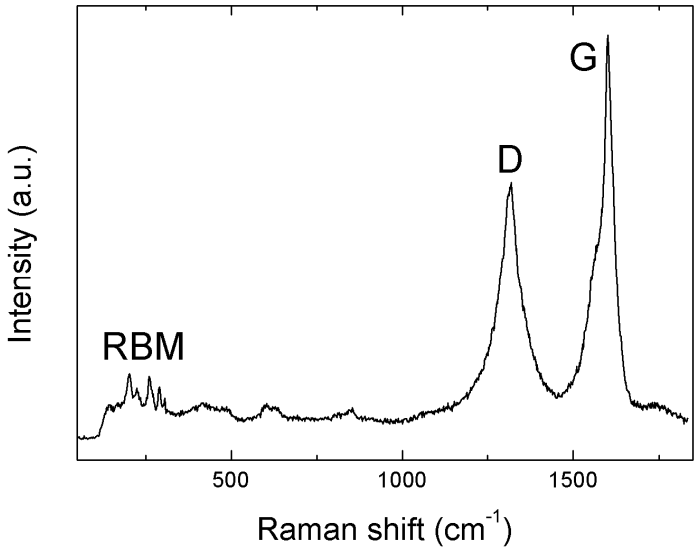

Figure 5. Raman spectrum of HiPCO nanotubes recovered after pressure cycling to 30 GPa. RBM, D- and G-band are indicated.

4. Conclusions

Peculiarities in pressure dependence of the resistance of HiPCO SWCNTs were observed at certain pressures which we relate to a structural transition – sequential collapse of the nanotubes. The collapse pressures are defined by CNT diameters. This transformation is accompanied by the I_D/I_G ratio increase in the Raman spectrum of the sample recovered after exposure to 30 GPa of non-hydrostatic pressure which is indicative of a high density of structural defects generated in the CNTs which have undergone collapse during the pressure cycling. The RBM band recovery implies a complete reversibility of the structural transitions and no CNT polymerization in the studied pressure range. Further experiments are required to ascertain the observed character of R(T) and probe structural stability of small (below 1 nm) diameter SWCNTs.

Acknowledgments

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